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# Theoretical study on the piezoelectric performance of lead-free 1–3-type composites

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The paper is devoted to the analysis of high-performance piezo-composites based on lead-free ferroelectric single crystals. The composite consists of parallelepiped-shaped single-crystal rods which are surrounded by a laminar polymer matrix, and the composite as a whole is described by 1–2–2 connectivity. Such a composite structure promotes high piezoelectric sensitivity and hydrostatic response. Of particular interest are piezoelectric coefficients  $g_{33}^*$  and  $h_{33}^*$ , squared figure of merit  $d_{33}^* g_{33}^*$ , electromechanical coupling factor  $k_t^*$  at the thickness-mode oscillation, and hydrostatic parameters  $g_h^*$  and  $d_h^* g_h^*$ . The influence of the laminar matrix on the aforementioned parameters is studied in a wide volume-fraction range. Examples of maxima and large anisotropy

of some effective parameters are discussed for the 1–2–2 composites based on  $[\text{Li}_x(\text{K}_{1-y}\text{Na}_y)_{1-x}](\text{Nb}_{1-z}\text{Ta}_z)\text{O}_3\text{:Mn}$  single crystals. The role of elastic properties of the laminar matrix in achieving large hydrostatic parameters and piezoelectric anisotropy of these composites is emphasised. Their effective parameters are compared to those of composites based on the lead-containing relaxor-ferroelectric single crystals and to specific parameters of poled textured ceramics. Advantages of the studied composites over the relaxor-ferroelectric-based composites and textured ceramics open up new possibilities to apply the 1–3-type lead-free composites as active elements of piezoelectric sensors, hydrophones, energy-harvesting, and transducer devices.

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## 1 Introduction

As is known from the literature, the overwhelming majority of ferroelectrics (FE) ceramics and single crystals (SCs) which exhibit high electromechanical coupling and important physical properties are lead-containing materials [1, 2] which unfortunately have the potential to pollute the environment. Research trends to discover an appropriate alternative to lead-containing FE and piezoelectric materials have been important in the last decade [3–6]. Among the promising materials that can be used as lead-

free FEs are polycrystalline ceramics and SCs based on alkali niobates. For instance, the longitudinal piezoelectric coefficient  $d_{33}$  of various poled (K, Na, Li)(Nb, Ta, Sb)O<sub>3</sub> [3], (K, Na, Li)(Nb, Sb)O<sub>3</sub> [5], (K, Li)(Nb, Ta, Sb)O<sub>3</sub> [6] and (K, Na)NbO<sub>3</sub>-based [4] ceramics can be found in the range from  $\sim 200$  pC N<sup>-1</sup> to 300 pC N<sup>-1</sup> at room temperature. In poled samples of textured (K, Na, Li)(Nb, Ta, Sb)O<sub>3</sub> ceramics, the value of  $d_{33} = 416$  pC N<sup>-1</sup> [3] is achieved. A ferroelectric nanostructured Mn-modified (K<sub>0.5</sub>Na<sub>0.5</sub>)NbO<sub>3</sub> ceramic is characterised by the piezoelectric coefficients  $d_{33} = 340$  pC N<sup>-1</sup>

and  $g_{33} = 220 \text{ mV}\cdot\text{m}\cdot\text{N}^{-1}$  and an anisotropy factor  $d_{33} / |d_{31}| \approx 21$  [7]. Of independent interest are domain-engineered FE SCs based on alkali niobates-tantalates with optimised electromechanical properties. These SCs are characterised [8–10] by relatively large piezoelectric coefficients  $d_{ij}$  and electromechanical coupling factors  $k_{ij}$ . For example, the piezoelectric coefficients of some (K, Na, Li)(Nb, Ta)O<sub>3</sub>-based SCs [10] poled along the perovskite unit-cell [001] direction exceed the typical values of  $d_{33} \approx 400\text{--}500 \text{ pC N}^{-1}$  and  $g_{33} \approx 30\text{--}40 \text{ mV}\cdot\text{m}\cdot\text{N}^{-1}$  of numerous FE ceramics based on Pb(Zr, Ti)O<sub>3</sub> [1, 11] with compositions near the morphotropic phase boundaries. However the aforementioned  $d_{33}$  values are smaller than those of domain-engineered relaxor-FE SCs such as  $(1 - x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$  (PMN- $x$ PT) and  $(1 - x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$  [12, 13]. Examples of full sets of electromechanical constants of the [001]-poled lead-free  $[\text{Li}_x(\text{K}_{1-y}\text{Na}_y)_{1-x}](\text{Nb}_{1-z}\text{Ta}_z)\text{O}_3$ :Mn and lead-containing PMN-0.33PT SCs are shown in Table 1. We add that both the SC compositions are located close to the morphotropic phase boundary.

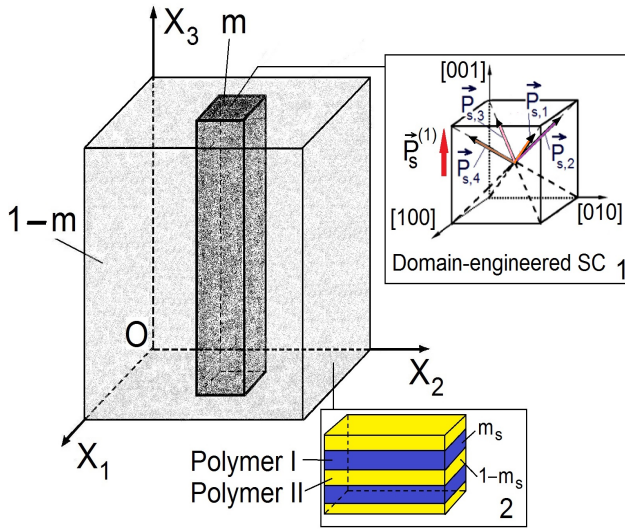
An example of using the domain-engineered lead-free SC as an active component of a 1-3-type composite was first discussed in work [18] where a high piezoelectric sensitivity associated with the piezoelectric coefficients  $g_{33}^*$  and  $g_h^*$  and related figures of merit was highlighted. We remind the reader that 1-3 connectivity in a piezo-active composite [19] relates to the presence of a system of long aligned piezoelectric rods (continuous along one co-ordinate axis) in a large matrix (continuous along three co-ordinate axes). The piezoelectric performance of a lead-free 1-3 ceramic / polymer composite studied in work [20] showed that such a material is of interest due to its electromechanical coupling factor  $k_t^*$ , piezoelectric coefficient  $g_{33}^*$ , and acoustic impedance  $Z^*$ . The ferroelectric ceramic used

to form the piezoelectric rods of the 1-3 composite had a nominal composition expressed by the formula  $(\text{Na}_{0.535}\text{K}_{0.485})_{0.914}\text{Li}_{0.086}(\text{Nb}_{0.942}\text{Ta}_{0.058})\text{O}_3$  [20].

A modification of the 1-3 composite structure, especially the matrix surrounding the piezoelectric rods, may lead to improved parameters, see, e.g. Refs. 15, 21 and 22. To the best of our knowledge, lead-free 1-3-type composites have yet to be studied in the context of the improvement of their parameters for potential piezotechnical applications. It is also important and timely to show advantages of the lead-free composites over their lead-containing counterparts such as 1-3-type composites based on PMN- $x$ PT SCs [23]. Below we discuss the role of the SC and polymer components in forming the piezoelectric performance and hydrostatic response of the 1-3-type composite wherein the matrix exhibits specific elastic properties.

## 2 Model of the composite, its components and effective properties

In our study, the 1-3-type composite contains a system of ferroelectric domain-engineered SC rods in the form of rectangular parallelepipeds with square bases (Fig. 1). These parallelepipeds are continuous in the  $OX_3$  direction, and their lateral faces are parallel to the  $(X_1OX_3)$  and  $(X_2OX_3)$  planes. It is assumed that each SC rod poled along the [001] direction of the perovskite unit cell is split into domains with spontaneous polarisation vectors  $\mathbf{P}_{s,1}$ ,  $\mathbf{P}_{s,2}$ ,  $\mathbf{P}_{s,3}$ , and  $\mathbf{P}_{s,4}$ , see the inset 1 of Fig. 1. The main crystallographic axes X, Y and Z of each SC rod are oriented as follows:  $X \parallel OX_1$ ,  $Y \parallel OX_2$  and  $Z \parallel \mathbf{P}_s^{(1)} \parallel OX_3$ , where  $\mathbf{P}_s^{(1)}$  is the spontaneous polarisation of the SC rod (or component as a whole), and  $OX_3$  is the poling axis for the composite sample. The SC rods are regularly distributed in the polymer matrix so that the centres of symmetry of the rod bases



**Figure 1** Schematic of the 1-2-2 SC / polymer I / polymer II composite with the planar microgeometry.  $(X_1X_2X_3)$  is the rectangular co-ordinate system,  $m$  is the volume fraction of the SC component, and  $m_s$  is the volume fraction of polymer I in the laminar matrix

form a simple square lattice in the  $(X_1OX_2)$  plane. The matrix that surrounds the SC rods consists of two polymer components, i.e., *polymer I* and *polymer II* in the form of layers with interfaces that are parallel to the  $(X_1OX_2)$  plane, see the inset 2 in Fig. 1. These layers are distributed regularly along the  $OX_3$  axis. Hereafter we use the term '*polymer I*' to denote a component with a larger stiffness, and the term '*polymer II*' is related to a component with a smaller stiffness in the laminar matrix. This matrix is characterised by 2-2 connectivity in terms of work [19, 21], and the 1-3-type composite as a whole is characterised by 1-2-2 connectivity. It is assumed that electrodes applied to the composite sample shown in Fig. 1 are parallel to the  $(X_1OX_2)$  plane.

The effective properties of the 1-2-2 composite are determined by means of the matrix method [14, 20, 21]. In the first stage, this method is applied to the laminar matrix, and boundary conditions for components of mechanical and electric fields [20] are taken into account at interfaces  $x_3 = \text{const}$ . The averaging procedure is carried out for the

properties of the polymer components, and the effective properties of the laminar matrix depend on a volume fraction  $m_s$  of *polymer I*. In the second stage, the averaging procedure is performed for the system "rods – matrix", and the aforementioned boundary conditions are applied to interfaces  $x_1 = \text{const}$  and  $x_2 = \text{const}$  (Fig. 1) by taking into account the boundary conditions described in monograph [20]. The volume fraction of SC,  $m$ , is a parameter on which the properties are now averaged. Such an averaging procedure is performed under the condition that the thickness of each polymer layer of the matrix is much smaller than the linear sizes of the SC rod base in the  $(X_1OX_2)$  plane, i.e., the system of the SC rods is surrounded by a laminar matrix with the effective (or homogenised) properties that have been determined in the first stage.

As a result of averaging, we find the effective electromechanical properties of the 1-2-2 composite. In the present study, these properties are characterised by the effective piezoelectric coefficients  $d_{ij}^*$ , elastic compliances  $s_{ab}^{*E}$  at electric field  $E = \text{const}$  and dielectric permittivities  $\epsilon_{pp}^{*\sigma}$  at mechanical stress  $\sigma = \text{const}$ . Hereafter with the asterisk (\*), we denote the effective properties and parameters of the studied composite. We remind the reader that the aforementioned properties are involved in the following equations of a piezoelectric medium [20, 24]:

$$\xi_a = s_{ab}^{*E} \sigma_b + d_{ia}^* E_i \text{ and } D_i = d_{ij}^* \sigma_j + \epsilon_{ir}^{*\sigma} E_r. \quad (1)$$

In Eqs. (1),  $\xi_a$ ,  $\sigma_b$ ,  $E_i$ , and  $D_i$  are mechanical strain, mechanical stress, electric field, and electric displacement, respectively.

The effective properties from Eqs. (1) and related parameters of the 1-2-2 composite are regarded as functions of the volume fractions  $m$  and  $m_s$ , and they can be varied in the range from 0 to 1. At  $m_s = 0$  or 1, we obtain



a 1–3 SC / polymer composite whose effective properties were studied earlier; see, e.g. Refs. 21 and 23.

The components that are of interest for our analysis and comparison are shown in Table 1, and their electromechanical constants are used in our evaluations. The lead-free KNNTL:Mn SC is of particular interest due to the large piezoelectric coefficients  $g_{ij}$  and  $h_{ij}$  and planar electromechanical coupling factor (ECF)  $k_p$ . It is seen from data in Table 1 that an unusual piezoelectric anisotropy is observed, i.e., conditions

$$|e_{31}| > e_{33} \text{ and } |h_{31}| > h_{33} \quad (2)$$

hold for the KNNTL:Mn SC at the relatively small ratio  $d_{33} / |d_{31}| = 2.10$ ; as shown by the data in Table 1. The PMN–0.33PT SC is regarded as a highly piezo-active lead-containing counterpart whose piezoelectric properties are characterised by validity of the condition

$$e_{33} / |e_{31}| = h_{33} / |h_{31}| > 5 \quad (3)$$

at  $d_{33} / |d_{31}| = 2.12$  (see data Table 1). We also consider three piezo-passive isotropic polymers as components of the laminar matrix. Hereby polyethylene (PE) is the softest component of the laminar matrix and will be regarded as *polymer II* in our further analysis.

Taking into account the effective properties of the composite  $d_{ij}^*(m, m_s)$ ,  $s_{ab}^{*E}(m, m_s)$  and  $\epsilon_{pp}^{*\sigma}(m, m_s)$ , we evaluate the effective piezoelectric coefficients  $g_{ij}^*(m, m_s)$ ,  $e_{ij}^*(m, m_s)$ , and  $h_{ij}^*(m, m_s)$ , and related parameters in accordance with formulae [20, 22]. In Section 3 we consider some examples of large parameters and specifics of their volume-fraction behaviour in the lead-free 1–2–2 composites.

### 3 Large effective parameters of 1–2–2 composites

#### 3.1 Piezoelectric coefficients $g_{3j}^*$ and $g_h^*$

The piezoelectric sensitivity of composites is often described in terms of their piezoelectric coefficients  $g_{ij}^*$  that link [24] an external mechanical stress field and an electric field due to a piezoelectric polarisation. As follows from our study, the presence of a laminar polymer matrix in the 1–2–2 composite (Fig. 1) influences the piezoelectric coefficients  $g_{3j}^*$  and their hydrostatic analog

$$g_h^* = g_{31}^* + g_{32}^* + g_{33}^* \quad (4)$$

Taking into account the microgeometry and macroscopic symmetry of the studied 1–2–2 composite, we represent its piezoelectric coefficients from Eq. (4) as

$$g_{3j}^* = d_{3j}^* / \epsilon_{33}^{*\sigma} \text{ and } g_h^* = d_h^* / \epsilon_{33}^{*\sigma},$$

**Table 1** Room-temperature elastic compliances  $s_{ab}^E$  (in  $10^{-12}$  Pa $^{-1}$ ), piezoelectric coefficients  $d_{ij}$  (in pC / N) and relative dielectric permittivity  $\epsilon_{pp}^\sigma / \epsilon_0$  of [001]-poled domain-engineered KNNTL:Mn<sup>a</sup> [10] and PMN–0.33PT [13] SCs, araldite [14], polyurethane [15], and polyethylene<sup>b</sup> [16, 17]

| Components                 | $s_{11}^E$ | $s_{12}^E$ | $s_{13}^E$ |       | $s_{44}^E$ | $s_{66}^E$ | $d_{31}$ | $d_{33}$ | $d_{15}$ | $\epsilon_{11}^\sigma / \epsilon_0$ | $\epsilon_{33}^\sigma / \epsilon_0$ |
|----------------------------|------------|------------|------------|-------|------------|------------|----------|----------|----------|-------------------------------------|-------------------------------------|
| KNNTL:Mn SC                | 33.4       | –7.36      | –25.8      | 57.7  | 12.8       | 13.5       | –260     | 545      | 66       | 400                                 | 650                                 |
| PMN–0.33PT SC <sup>c</sup> | 69.0       | –11.1      | –55.7      | 119.6 | 14.5       | 15.2       | –1330    | 2820     | 146      | 1600                                | 8200                                |
| Araldite                   | 216        | –78        | –78        | 216   | 588        | 588        | 0        | 0        | 0        | 4.0                                 | 4.0                                 |
| Polyurethane               | 401        | –149       | –149       | 401   | 1100       | 1100       | 0        | 0        | 0        | 3.5                                 | 3.5                                 |
| Polyethylene               | 1430       | –286       | –286       | 1430  | 3430       | 3430       | 0        | 0        | 0        | 2.3                                 | 2.3                                 |

<sup>a</sup>  $[\text{Li}_x(\text{K}_{1-y}\text{Na}_y)_{1-x}](\text{Nb}_{1-z}\text{Ta}_z)\text{O}_3:\text{Mn}$ , where  $x = 0.06$ ,  $y = 0.1–0.3$ ,  $z = 0.07–0.17$ , and the level of Mn doping is 0.25 mol. %, see Ref. 10.

This SC is characterised by  $4mm$  symmetry, piezoelectric coefficients  $g_{33} = 94.7$  and  $g_{31} = -45.2$  (in mV·m·N $^{-1}$ ),  $e_{33} = 4.53$  and  $e_{31} = -5.50$  (in C·m $^{-2}$ ),  $h_{33} = 106$  and  $h_{31} = -129$  (in  $10^8$  V·m $^{-1}$ ), squared figure of merit  $d_{33}g_{33} = 51.6 \cdot 10^{-12}$  Pa $^{-1}$ , and electromechanical coupling factors  $k_t = 0.491$  (thickness oscillation mode) and  $|k_p| = 0.951$  (planar oscillation mode).

<sup>b</sup> Elastic properties of monolithic polyethylene are taken from work [16], and dielectric properties are taken from work [17].

<sup>c</sup> This SC is characterised by  $4mm$  symmetry, piezoelectric coefficients  $g_{33} = 38.9$  and  $g_{31} = -18.3$  (in mV·m·N $^{-1}$ ),  $e_{33} = 20.3$  and  $e_{31} =$

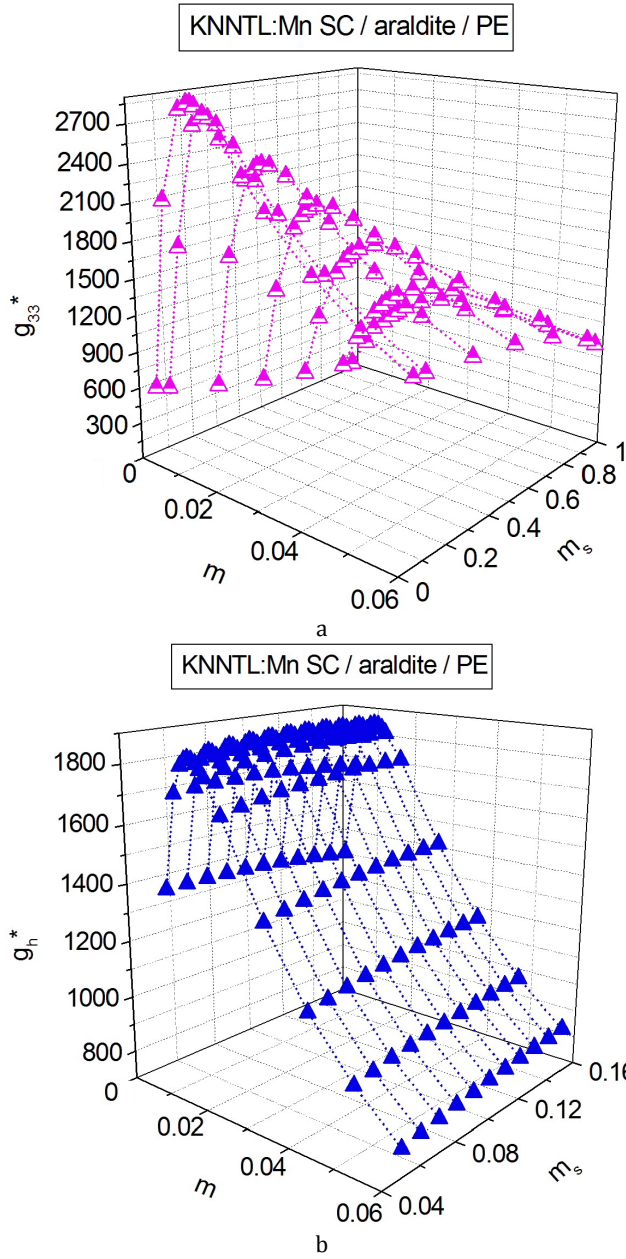
(5)

where  $j = 1, 2$  and  $3$ , and  $d_h^* = d_{31}^* + d_{32}^* + d_{33}^*$ . We add that equalities  $d_{31}^* = d_{32}^*$  and  $g_{31}^* = g_{32}^*$  hold because of the regular distribution of the SC rods from the  $4mm$  symmetry class in the laminar polymer matrix with  $\infty mm$  symmetry, and therefore, the hydrostatic piezoelectric coefficients from Eqs. (4) and (5) can be written as  $d_h^* = d_{33}^* + 2d_{31}^*$  and  $g_h^* = g_{33}^* + 2g_{31}^*$ .

The piezoelectric coefficients  $g_{3j}^*$  and  $g_h^*$  are characterised by extremum points at volume fractions of SC  $m \ll 1$  (Figs. 2 and 3), and this is a common feature of 1–3-type piezo-active composites [22, 23]. Such a feature is a result of the strong influence of the dielectric permittivity  $\epsilon_{33}^{*\sigma}$  from Eqs. (5) on  $g_{3j}^*$  and  $g_h^*$  at small volume fractions of SC, i.e., when its dielectric properties make a very small contribution to  $\epsilon_{33}^{*\sigma}$  and when the piezoelectric coefficients  $d_{3j}^*$  undergo considerable changes (e.g. rapid increase of  $d_{33}^*$  on increasing the volume fraction of SC) [21, 23] due to the system of the parallel SC rods in the relatively soft matrix. In Figs. 2 and 3 we do not present the behaviour of the piezoelectric coefficient  $g_{31}^*$  since it may be simply evaluated from the expression  $g_{31}^* = (g_h^* - g_{33}^*) / 2$ . In the 2D graphs shown in Figs. 2, d and e and 3, e, we show the behaviour of  $g_h^*$  near local max  $g_h^*$  at  $m_s = \text{const}$ .

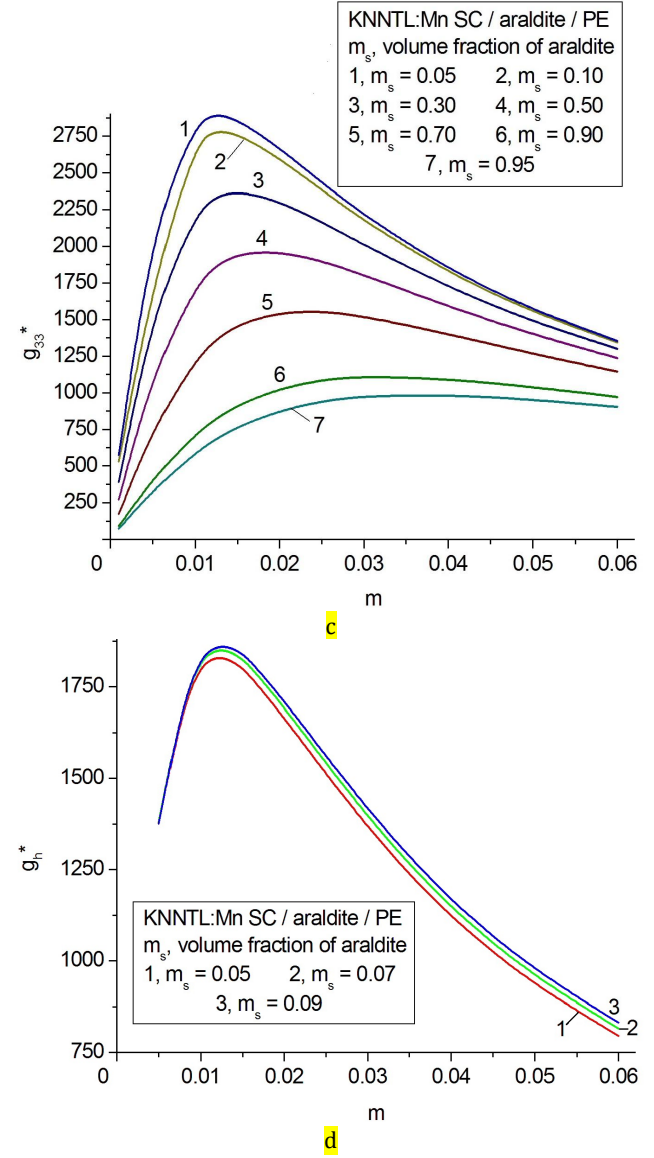
As follows from our data, local min  $g_{31}^*$  is achieved almost at a volume fraction  $m$  related to local max  $g_{33}^*$  at  $m_s = \text{const}$  (Figs. 2, a and 3, a). It is seen from Fig. 2, b that a diffuse max  $g_h^*$  is observed at  $m < 0.02$  and  $0.05 < m_s < 0.15$ , and decrease in  $g_h^*$  is related to an increase of the volume fraction of SC  $m$ . On comparing the hydrostatic piezoelectric coefficients  $g_h^*$  of the araldite- and polyurethane-containing composites, we

observe that the larger max  $g_h^*$  value is related to the araldite-containing composite, see Figs. 2, b and 3, b and data in Table 2. This is achieved despite the larger values of  $g_{33}^*$  in the polyurethane-containing composite (see Figs. 2, a and c, 3, a and c, and the 4th column in Table 2). The laminar matrix (inset 2 in Fig. 1), wherein the elastic properties of the polymer components differ to a smaller degree, promotes a larger piezoelectric coefficient  $g_{33}^*$  at  $m = \text{const}$ . Data on polymers from Table 1 suggest that a smaller difference is expected for the composite with the polyurethane / PE matrix. Data in Table 2 show that a difference between the  $g_{33}^*$  values calculated for the related composites at  $m_s = \text{const}$  and  $m = \text{const}$  can reach a few percent. However the  $g_{31}^*$  values calculated for the same composites at  $m_s = \text{const}$  and  $m = \text{const}$  can differ to a larger extent (see data in the 5th column of Table 2). For example, at  $m_s = 0.05$  and  $m = 0.012$  we see a 1% difference between  $g_{33}^*$  and a 14% difference between  $g_{31}^*$  of the studied 1–2–2 composites. On moving away from the max  $g_h^*$  point we also observe a considerable difference between the  $g_{31}^*$  values. For instance, at  $m_s = 0.10$  and  $m = 0.050$  this difference reaches 19% since almost equal  $g_{33}^*$  values of the same com-

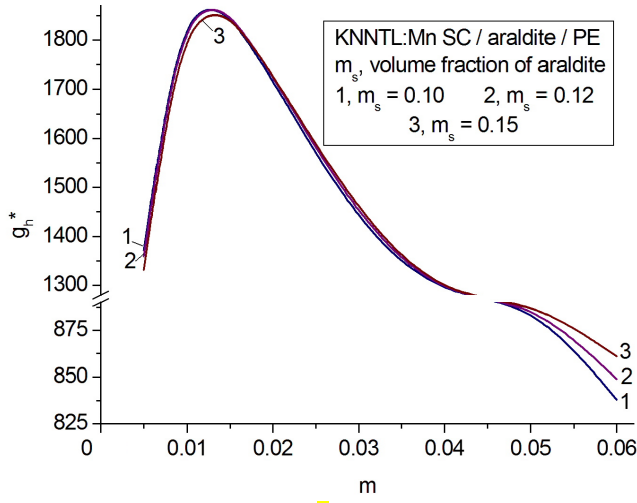


**Figure 2** Volume-fraction behaviour of the piezoelectric coefficients  $g_{33}^*$  (a and c, in  $\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ ) and  $g_h^*$  (b, d and e, in  $\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ ) of the 1-2-2 KNNTL:Mn SC / araldite / PE composite near local max  $g_{33}^*$  and max  $g_h^*$ , and relations between  $g_{3j}^*$  and  $g_h^*$  (f, in  $\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ ) at volume fractions of SC  $m = 0.05$  (curves 1–3 in graph f) and  $m = 0.10$  (curves 4–6 in graph f).

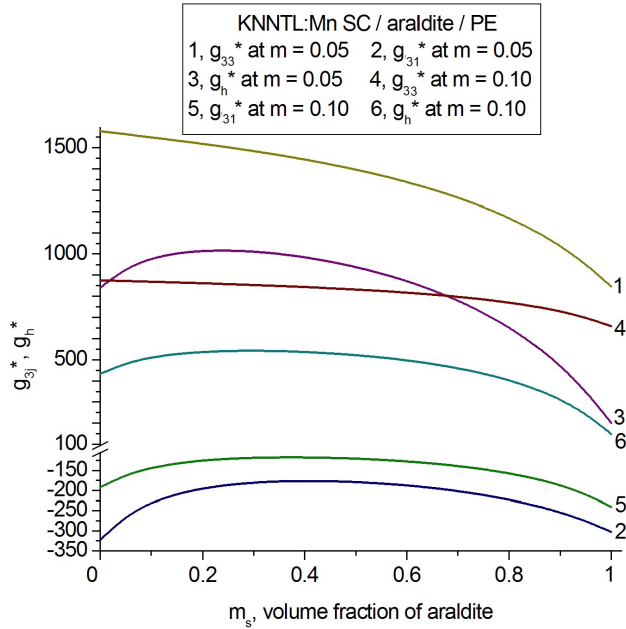
$m_s = \text{const.}$  This can lead to a larger  $g_h^*$  value even with a smaller contribution from  $g_{33}^*$  in Eq. (4). In our opinion, the transverse piezoelectric effect in the 1-2-2 composite plays the important role in forming the hydrostatic piezoelectric res-



posites are observed. Data from Table 2 suggest that in the araldite-containing composite (with the larger difference between the elastic properties of polymers), a smaller contribution from  $|g_{31}^*|$  into  $g_h^*$  is observed at



**Figure 2** (continued)



**Figure 2** (continued)

have been reported in the literature, where Choy et al. [25] manufactured the samples with low volume fractions of FE ceramic rods (approximately 0.033, 0.066 etc.), and therefore, the 1–3-type composite with volume fractions of SC  $0.03 < m < 0.1$  (Fig. 1) could be manufactured. To compare the piezoelectric coefficients from Eqs. (5), we consider the performance of the 1–2–2 composites based on the KNNTL:Mn SC at  $m = 0.05$  and  $0.10$ . The graphs in Fig. 2, d–f and 3, d and e show that a considerable dependence of  $g_h^*$  and  $g_{3j}^*$  on the volume fraction of polymer  $m_s$  is observed even at the volume fractions of SC  $m \leq 0.10$ . This means that the elastic anisotropy of the laminar matrix plays an important role in forming the piezoelectric sensitivity of the composite and, therefore, can influence its piezoelectric anisotropy. It should be added that local max  $g_h^*$  at  $m = 0.05$  can be found in the volume-fraction range  $0.2 < m_s < 0.3$  for both the composites, see curves 3 in Figs. 2, f and 3, e.

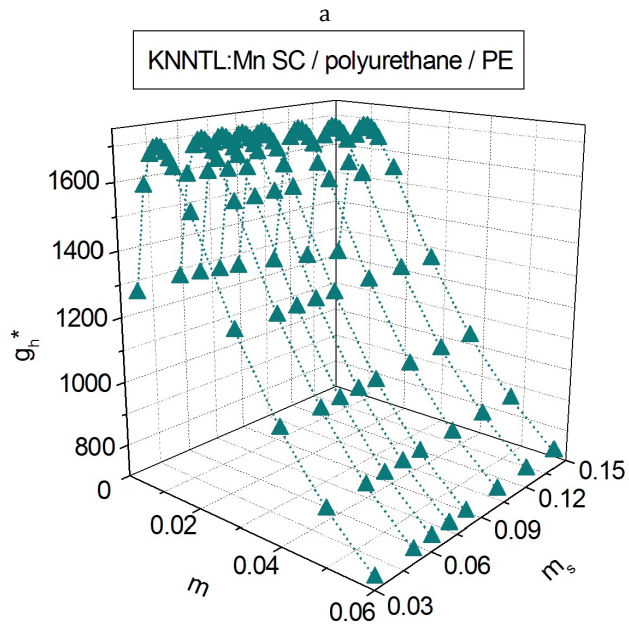
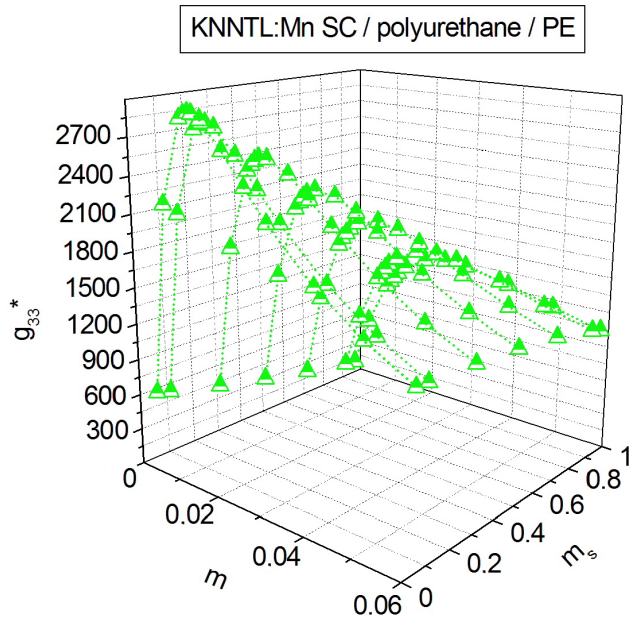
**3.2 Squared figures of merit  $(Q_{3j}^*)^2$  and  $(Q_h^*)^2$**  Squared strain–voltage figures of merit

$$(Q_{33}^*)^2 = d_{33}^* g_{33}^* \text{ and } (Q_{31}^*)^2 = d_{31}^* g_{31}^* \quad (6)$$

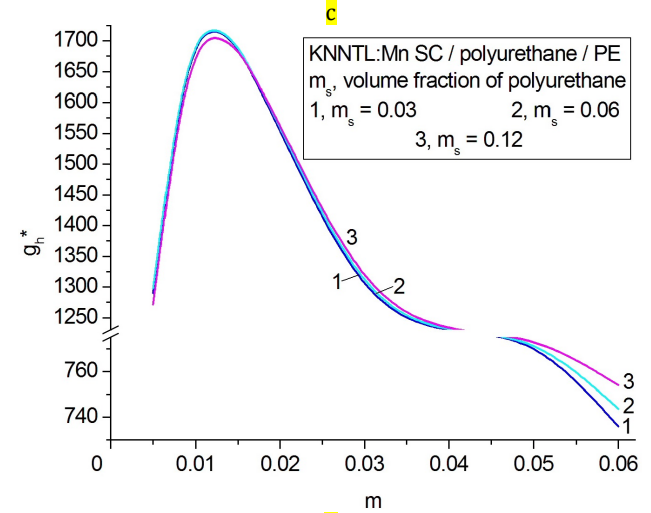
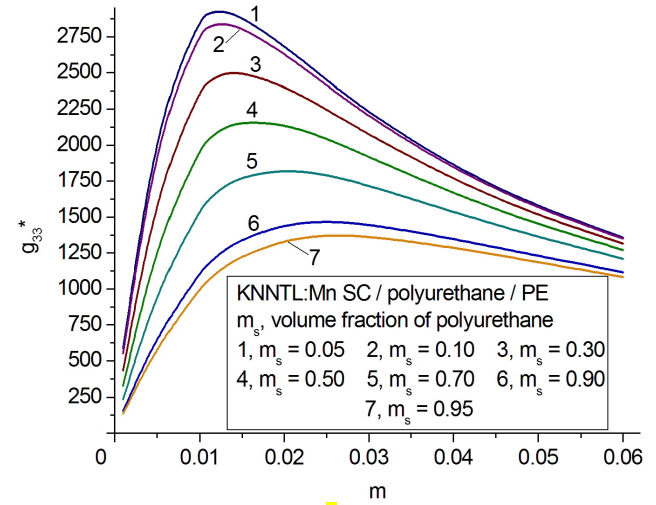
ponse, and this role is inseparably linked with the anisotropic elastic properties of the laminar matrix that influences mechanical and electric fields in the piezoelectric SC rods. We add that some features of these elastic properties will be discussed in Section 3.3.

The need for small volume fractions of SC  $m$  may be problematic in terms of ease of manufacturing of composites with the stable piezoelectric performance. Data on 1–3 ferroelectric ceramic / polymer composites





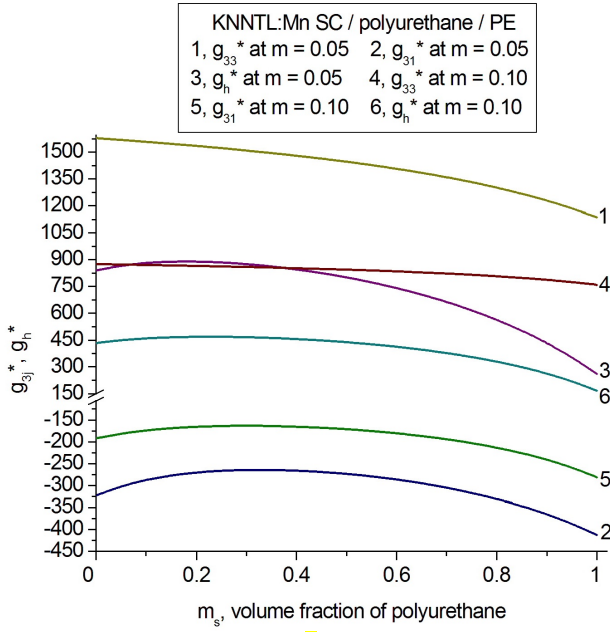
hydrostatic piezoelectric coefficients  $d_h^*$  and  $g_h^*$  from Eqs. (5) as follows:



**Figure 3** Volume-fraction behaviour of the piezoelectric coefficients  $g_{33}^*$  (a and c, in  $\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ ) and  $g_h^*$  (b and d, in  $\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ ) of the 1-2-2 KNNTL:Mn SC / polyurethane / PE composite near local max  $g_{33}^*$ , and relations between  $g_{3j}^*$  and  $g_h^*$  (e, in  $\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ ) at volume fractions of SC  $m = 0.05$  (curves 1-3 in graph e) and  $m = 0.10$  (curves 4-6 in graph e).

are concerned with the longitudinal and transverse piezoelectric effect, respectively. The hydrostatic analog of the parameters from Eqs. (6) is written in terms of the





**Figure 3** (continued)

**Table 2** Piezoelectric coefficients  $g_h^*$  and  $g_{3j}^*$  (in mV·m·N<sup>-1</sup>) of the 1–2–2 KNNTL:Mn SC / araldite / PE and KNNTL:Mn SC / polyurethane / PE near local max  $g_h^*$

| $m_s$                                     | $m$   | $g_h^*$ | $g_{33}^*$ | $g_{31}^*$ |
|---|-------|---------|------------|------------|
| KNNTL:Mn SC / araldite / PE composite     |       |         |            |            |
| 0.05                                      | 0.012 | 1830    | 2890       | -530       |
| 0.08                                      | 0.012 | 1860    | 2820       | -480       |
| 0.10                                      | 0.013 | 1860    | 2780       | -460       |
|   | 0.030 | 1420    | 2170       | -375       |
|   | 0.050 | 980     | 1550       | -285       |
| 0.14                                      | 0.013 | 1860    | 2690       | -415       |
| 0.18                                      | 0.013 | 1830    | 2610       | -390       |
| KNNTL:Mn SC / polyurethane / PE composite |       |         |            |            |
| 0.05                                      | 0.012 | 1720    | 2930       | -605       |
| 0.07                                      | 0.012 | 1720    | 2890       | -585       |
| 0.10                                      | 0.012 | 1710    | 2840       | -565       |
|   | 0.030 | 1280    | 2200       | -460       |
|   | 0.050 | 883     | 1560       | -339       |
| 0.14                                      | 0.013 | 1690    | 2770       | -540       |
| 0.16                                      | 0.013 | 1660    | 2710       | -525       |

<sup>a</sup> The  $m$  value at which local max  $g_h^*$  is achieved

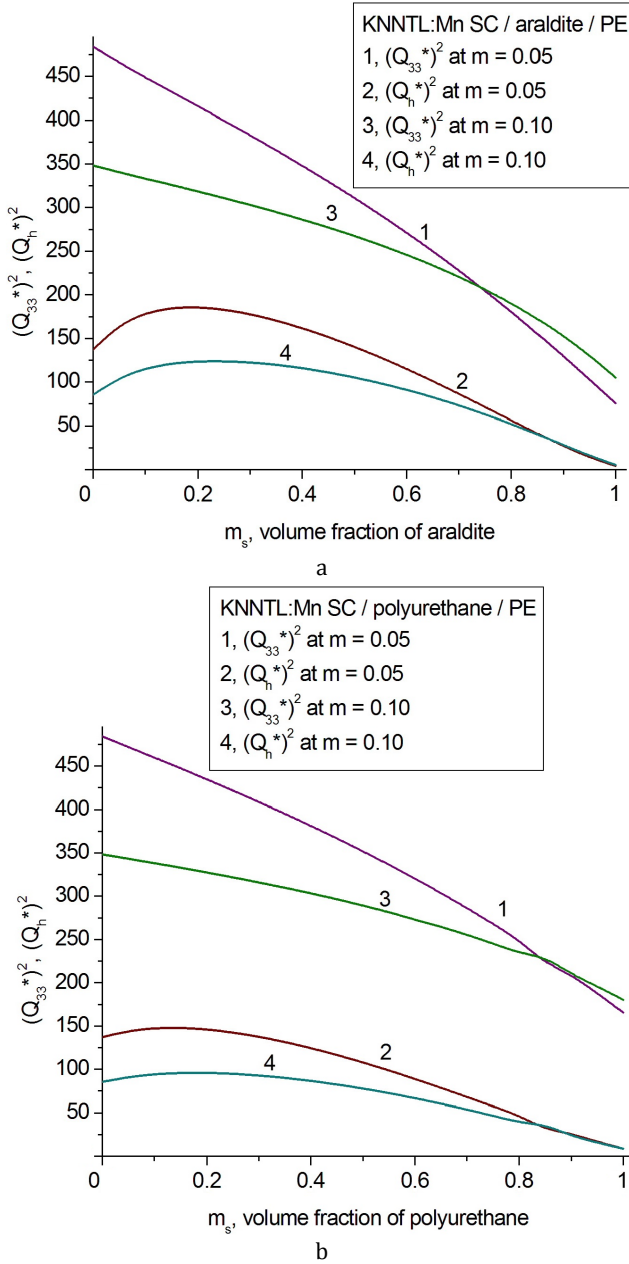
$$(Q_h^*)^2 = d_h^* g_h^* = (g_h^*)^2 \epsilon_{33}^{*\sigma}. \quad (7)$$

The squared figures of merit from Eqs. (6) and (7) are used to estimate the sensor signal-to-noise ratio of the composite and its piezoelectric sensitivity [18, 21, 22]. Examples of the volume-fraction behaviour of the squared figures of merit of the studied composites are graphically represented in Fig. 4.

Our comparison of Fig. 4, a to Fig. 2, f and Fig. 4, b to Fig. 3, e shows that there is a correlation between the piezoelectric coefficient  $g_{33}^*$  and the squared figure of merit  $(Q_{33}^*)^2$  from Eqs. (6) as well a correlation between  $g_h^*$  and  $(Q_h^*)^2$  from Eq. (7). We see the non-monotonic dependences of both  $g_h^*$  and  $(Q_h^*)^2$  on the volume fraction  $m_s$ . It seems probable that the piezoelectric coefficients  $g_{3j}^*$  play a dominating role in the determination of the figures merit from Eqs. (6) and (7) at SC volume fractions of  $m \leq 0.10$ , i.e., at relatively small dielectric permittivities  $\epsilon_{33}^{*\sigma}$ .

Irrespective of the polymer components in the laminar matrix, points of  $\max[(Q_h^*)^2]$  are located close to the volume fraction  $m_s = 0.2$ , see curves 2 and 4 in graphs of Fig. 4. As with local max  $g_h^*$  at  $m \leq 0.10$  (see Section 3.1), the larger value of local max  $[(Q_h^*)^2]$  is achieved in the presence of the araldite-containing laminar matrix, i.e., at the larger difference between the elastic properties of the polymer components.

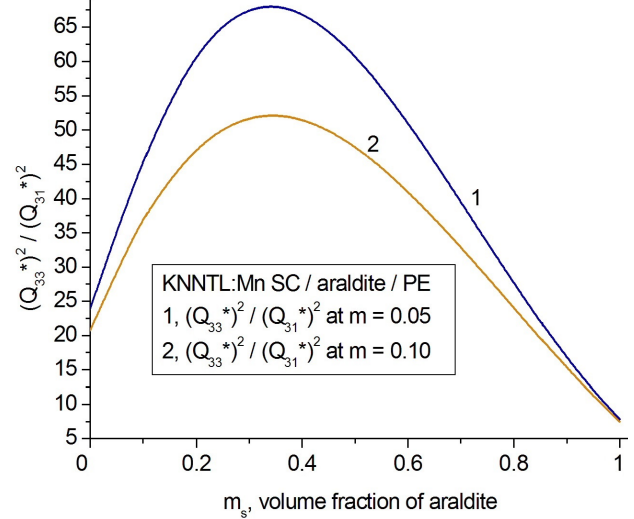
The large  $(Q_{33}^*)^2$  values that are achieved in the composites at  $m \leq 0.10$  (see curves 1 and 3 in Fig. 4) are compa-



**Figure 4** Relations between the squared figures of merit  $(Q_{33}^*)^2$  and  $(Q_h^*)^2$  (in  $10^{-12} \text{ Pa}^{-1}$ ) of the 1–2–2 KNNTL:Mn SC / araldite / PE (a) and KNNTL:Mn SC / polyurethane / PE (b) composites at volume fractions of SC  $m = 0.05$  (curves 1 and 2) and  $m = 0.10$  (curves 3 and 4).

red to the squared figure of merit  $(Q_{31}^*)^2$  (Fig. 5) to find the volume-fraction ranges where the longitudinal piezo-electric sensitivity is dominating. A comparison of curves 1 and 2 in Fig. 5 enables us to determine that the larger anisotropy of the squared figures of merit  $(Q_{3j}^*)^2$

)<sup>2</sup> from Eqs. (6) is achieved at a smaller volume fraction of SC  $m$  and in the volume-fraction range  $0.3 < m_s < 0.4$ . An increase of  $m$



**Figure 5** Anisotropy of the squared figures of merit  $(Q_{33}^*)^2 / (Q_{31}^*)^2$  of the 1–2–2 KNNTL:Mn SC / araldite / PE composite at volume fractions of SC  $m = 0.05$  (curve 1) and  $m = 0.10$  (curves 2).

leads to the smaller  $(Q_{33}^*)^2 / (Q_{31}^*)^2$  ratio, and this is accounted for by the influence of the SC component with a relatively small ratio of the piezoelectric coefficients. We remind the reader that the [001]-poled KNNTL:Mn SC is characterised by the ratio  $g_{33} / |g_{31}| = 2.10$ , see data in Table 1.

### 3.3 Elastic properties of the matrix and piezoelectric anisotropy of the composite

In Sections 3.1 and 3.2 we considered the effective parameters of the composite at volume fractions of SC  $m \leq 0.10$ . In this case, the elastic and dielectric properties of the laminar matrix can influence the electromechanical properties of the composite, its piezoelectric sensitivity, and figures of merit to a large extent.

We start from relations that describe the piezoelectric effect, its anisotropy and hydrostatic response in the composite with  $4mm$  symmetry. As seen from Eqs. (5), the

piezoelectric coefficients  $d_{3j}^*$  and  $g_{3j}^*$  are linked by the dielectric permittivity  $\epsilon_{33}^{*\sigma}$ . However, on analysis of the anisotropic piezoelectric effect in the 1–3-type composite, it is easier to use the piezoelectric coefficients  $e_{3j}^*$ . As is known from work [21, 26], the 1–3-type composite is characterised by almost linear dependences of  $e_{3j}^*$  and  $\epsilon_{33}^{*\sigma}$  on the volume fraction of the piezoelectric rods while this volume fraction remains relatively small. In the same volume-fraction range, the piezoelectric coefficients  $e_{3j}^*$  of the composite obey the condition

$$e_{33}^* / |e_{31}^*| \gg 1. \quad (8)$$

The piezoelectric coefficients  $d_{3j}^*$  are written in terms of  $e_{3j}^*$  [21, 24] as follows:

$$d_{31}^* = e_{31}^* (s_{11}^{*E} + s_{12}^{*E}) + e_{33}^* s_{13}^{*E} \text{ and } d_{33}^* = 2 e_{31}^* s_{13}^{*E} + e_{33}^* s_{33}^{*E}. \quad (9)$$

Based on Eqs. (5) and (9) and taking into account the condition (8), we represent the hydrostatic piezoelectric coefficients of the composite in the following form:

$$d_h^* \approx e_{33}^* (s_{33}^{*E} + 2 s_{13}^{*E}) \text{ and } g_h^* \approx e_{33}^* (s_{33}^{*E} + 2 s_{13}^{*E}) / \epsilon_{33}^{*\sigma}. \quad (10)$$

At the small volume fraction of the piezoelectric rods, the sum  $s_{33}^{*E} + 2 s_{13}^{*E}$  from Eqs. (10) will approach the similar sum  $s_{33}^{(m)} + 2 s_{13}^{(m)}$  related to the laminar matrix. The anisotropy factor of the composite is then represented as

$$d_{33}^* / |d_{31}^*| = g_{33}^* / |g_{31}^*| \approx s_{33}^{(m)} / |s_{13}^{(m)}|. \quad (11)$$

Equation (11) enables us to link the piezoelectric anisotropy of the composite and the elastic anisotropy of its laminar matrix.

The elastic properties of the laminar matrix depend on the volume fraction  $m_s$  of *polymer I*, see Fig. 6. Of specific interest are curves 3 and 4. It is seen that the elastic compliance  $s_{13}^{(m)}$  of both the laminar matrices undergoes considerable changes at  $m_s < 0.3$ , and  $s_{33}^{(m)}$  monotonously decreases in the whole  $m_s$  range. Such a behaviour of the elastic compliances  $s_{a3}^{(m)}$  (see curves 3 and 4 in Fig. 6) suggests that a compromise  $m_s$  range can be found where  $|s_{13}^{(m)}|$  remains relatively small and  $s_{33}^{(m)}$  remains relatively large. Earlier we mentioned the volume-fraction ranges  $0.2 < m_s < 0.3$  and  $0.3 < m_s < 0.4$ : the first range is concerned with local max  $g_h^*$  at  $m = 0.05$  (see Section 3.1), and the latter range is concerned with the large anisotropy of the squared figures of merit  $(Q_{3j}^*)^2$ ; see Section 3.2.

Thus, Eq. (11) and Fig. 6 are to be taken into account at the interpretation of the piezoelectric anisotropy in the studied composites based on the KNNTL:Mn SC. An important example of the large piezoelectric anisotropy of these composites is illustrated by Fig. 7. Hereby we consider validity of the following conditions:

$$d_{33}^* / |d_{31}^*| = g_{33}^* / |g_{31}^*| \geq 5 \quad (12)$$

and

$$k_t^* / |k_p^*| \geq 5. \quad (13)$$

Conditions (12) and (13) are concerned with the anisotropy factors that are important for energy-harvesting and other piezotechnical applications [27]. In Eq. (13),

$$k_t^* = e_{33}^* / (c_{33}^{*D} \epsilon_{33}^{*\xi})^{1/2} \quad (14)$$

and

$$k_p^* = d_{31}^* \sqrt{\frac{2}{\epsilon_{33}^{*\sigma} (s_{11}^{*E} + s_{12}^{*E})}} \quad (15)$$

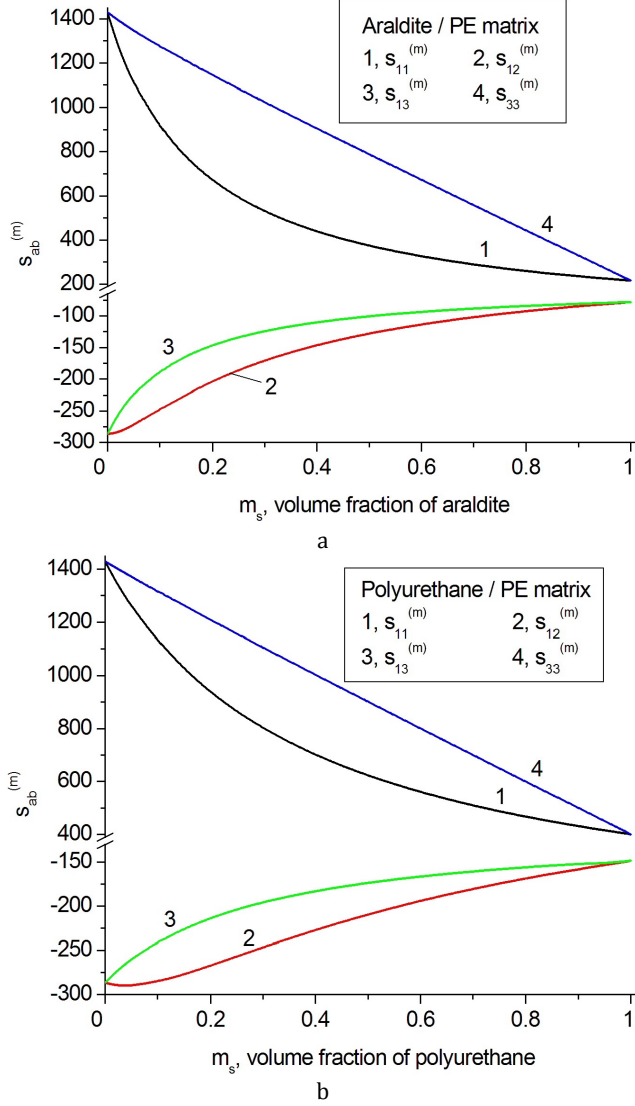
are thickness and planar ECFs, respectively. The ECFs from Eqs. (14) and (15) are used to characterise an

displacement  $D = \text{const}$  and dielectric permittivity at mechanical strain  $\xi = \text{const}$ , respectively. Based on Eqs. (14) and (15), we represent the ECF anisotropy factor  $k_t^* / k_p^*$  as

$$k_t^* / k_p^* = \sqrt{\epsilon_{33}^{*\sigma} / (2\epsilon_{33}^{*\xi})} \sqrt{(s_{11}^{*E} + s_{12}^{*E}) / c_{33}^{*D} / s_{13}^{*E}}. \quad (16)$$

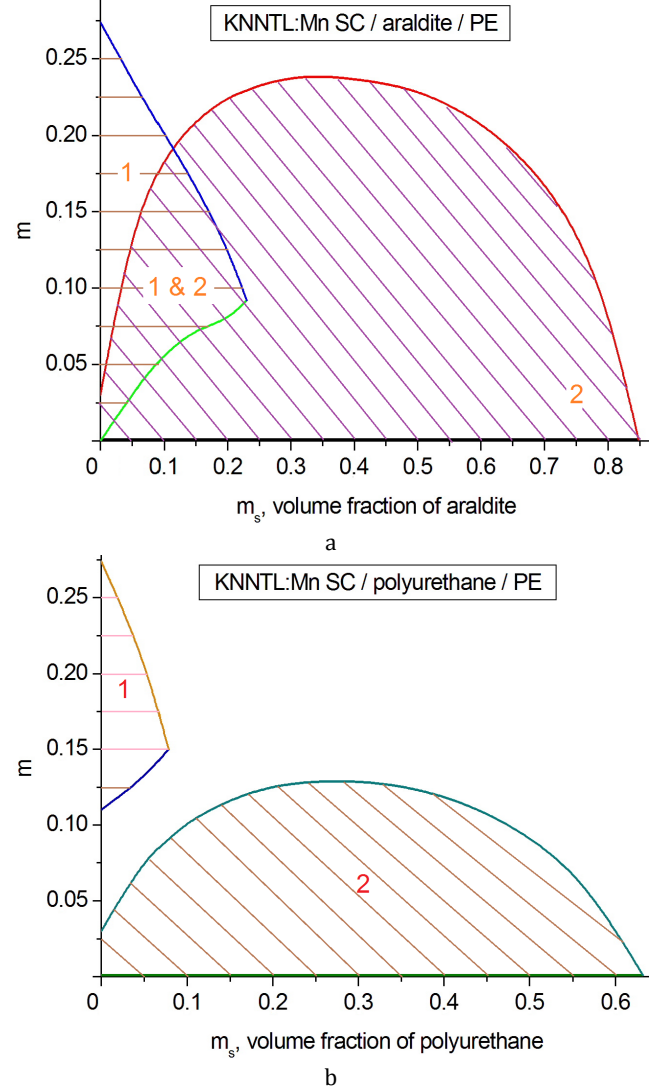
Taking into account the fact that conditions (12) and (13) to achieve a large piezoelectric anisotropy hold at the relatively small volume fractions  $m$  (see area 1 & 2 in Fig. 7, a), we use the following relations to simplify Eq. (16):

$s_{ab}^{*E} \approx s_{ab}^{(m)}$  and  $c_{33}^{*D} \approx 1 / s_{33}^{(m)}$ . After simplification, we write



**Figure 6** Volume-fraction ( $m_s$ ) dependence of elastic compliances  $s_{ab}^{(m)}$  (in  $10^{-12} \text{ Pa}^{-1}$ ) of the laminar matrix of the composite, see Fig. 1. Graphs a and b are related to the matrices wherein polymer I is araldite and polyurethane, respectively.

effectiveness of the energy conversion in 1–3 composites that are applied as piezo-active elements of transducers [24, 26]. In Eq. (14),  $c_{33}^{*D}$  and  $\epsilon_{33}^{*\xi}$  are the elastic modulus at electric



**Figure 7** Regions of the large piezoelectric anisotropy in the 1–2–2 KNNTL:Mn SC / araldite / PE (a) and 1–2–2 KNNTL:Mn SC / polyurethane / PE (b) composites: 1, region of the valid condition (13), and 2, region of the valid condition (12).

the ECF anisotropy factor as follows:

$$k_t^* / k_p^* \approx \sqrt{\varepsilon_{33}^{*\sigma} / (2\varepsilon_{33}^{*\xi})} s_{anis}, \quad (17)$$

where

**Table 3** Relations between elastic compliances  $s_{ab}^{(m)}$  of the laminar matrix<sup>a</sup> and anisotropy factors  $k_t^* / k_p^*$  and  $d_{33}^* / d_{31}^*$  of the

1–2–2 KNNTL:Mn SC / polymer I / polymer II composite<sup>b</sup> at the volume fraction of SC  $m \ll 1$

| Polymer I / polymer II | Volume fraction of polymer I $m_s$ | $s_{anis}$ , laminar matrix | $s_{33}^{(m)} / s_{13}^{(m)}$ , laminar matrix | Volume fraction of SC $m$ | $k_t^* / k_p^*$ , composite | $d_{33}^* / d_{31}^*$ , composite |
|------------------------|------------------------------------|-----------------------------|--|---------------------------|-----------------------------|-----------------------------------|
| Araldite / PE          | 0.05                               | -4.96                       | -6.03  | 0.08                      | -5.04                       | -5.63                             |
|                        | 0.10                               | -4.99                       | -6.83  | 0.08                      | -5.09                       | -6.35                             |
|                        | 0.15                               | -5.00                       | -7.43  | 0.08                      | -5.08                       | -6.88                             |
|                        | 0.20                               | -5.00                       | -7.85  | 0.08                      | -5.04                       | -7.25                             |
|                        | 0.25                               | -4.97                       | -8.12  | 0.08                      | -4.88                       | -7.49                             |
|                        | 0.30                               | -4.90                       | -8.27  | 0.08                      | -4.72                       | -7.62                             |
| Polyurethane / PE      | 0.05                               | -4.44                       | -5.28  | 0.05                      | -4.37                       | -5.20                             |
|                        | 0.10                               | -4.39                       | -5.48  | 0.05                      | -4.30                       | -5.43                             |
|                        | 0.15                               | -4.31                       | -5.60  | 0.05                      | -4.20                       | -5.59                             |
|                        | 0.20                               | -4.22                       | -5.67  | 0.05                      | -4.07                       | -5.69                             |
|                        | 0.25                               | -4.12                       | -5.69  | 0.05                      | -3.95                       | -5.72                             |
|                        | 0.30                               | -4.01                       | -5.66  | 0.05                      | -3.91                       | -5.71                             |

<sup>a</sup> See the inset 2 in Fig. 1

$$s_{anis} = \sqrt{(s_{11}^{(m)} + s_{12}^{(m)}) / s_{33}^{(m)}} / s_{13}^{(m)}. \quad (18)$$

Data from Table 3 show that the relations between the elastic compliances of the laminar matrix, namely,  $s_{anis}$  from Eq. (18) and  $s_{33}^{(m)} / s_{13}^{(m)}$ , correlate with the anisotropy factors  $k_t^* / k_p^*$  and  $d_{33}^* / d_{31}^*$  of the composite, respectively. The  $\sqrt{\varepsilon_{33}^{*\sigma} / (2\varepsilon_{33}^{*\xi})}$  factor from Eq. (17) is concerned with the longitudinal dielectric response of the composite and undergoes minor changes at volume fractions  $m \ll 1$  and variations of  $m_s$ . A comparison of data from the 3rd and 6th columns of Table 3 enables us to emphasise the key role of the elastic properties of the laminar matrix in achieving a large anisotropy of ECFs from Eq. (16). The  $s_{anis}$  factor from Eqs. (17) and

(18) enables us to interpret regions 1 in Fig. 7, especially where the interference of regions 1 and 2 is observed (see Fig. 7, a and 5th–7th columns in the first part of Table 3). As in Sections 3.1 and 3.2, we underline the advantage of the araldite-containing composite over the polyurethane-containing composite because conditions (12) and (13) for the large anisotropy hold simultaneously, see the 1 & 2 area in Fig. 7,

a. Here it is important to mention the ECF anisotropy factor of the KNNTL:Mn SC for comparison. According to data from Table 1 for this SC,  $k_t / |k_p| = 0.516$ , i.e., an order-of-magnitude smaller than the  $k_t^* / k_p^*$  values related to the araldite-containing composite; see 6th column in the first part of Table 3.

### 3.4 Piezoelectric coefficient $h_{33}^*$ and electromechanical coupling factor $k_t^*$ The studied

1–2–2 composites based on the KNNTL:Mn SC are also of interest due to large values of the thickness ECF  $k_t^*$  from Eq. (14), piezoelectric coefficient

$$h_{33}^* = e_{33}^* / \varepsilon_{33}^{*\xi} \quad (19)$$



and related anisotropy factor  $|h_{33}^*|/|h_{31}^*| = |e_{33}^*|/|e_{31}^*|$ . The piezoelectric coefficients  $h_{3j}^*$  link mechanical strain and electric field due to the piezoelectric effect [24]. A large anisotropy of  $h_{3j}^*$  is achieved in a wide volume-fraction ( $m$ ) range, and it is the common feature of the 1–3-type composites [21] with aligned piezoelectric rods. Comparing Eqs. (14) and (19), it is easy to show that the piezoelectric coefficient  $h_{33}^*$  and thickness ECF  $k_t^*$  are linked as follows:

$$k_t^* = h_{33}^* (\epsilon_{33}^{*\xi} / c_{33}^{*D})^{1/2}. \quad (20)$$

A monotonic increase of the dielectric permittivity  $\epsilon_{33}^{*\xi}$  and elastic modulus  $c_{33}^{*D}$  from Eq. (20) on increasing the volume fraction of the piezoelectric rods ( $m$  in the case of the 1–2–2 composite) promotes similar configurations of the volume-fraction dependences of  $k_t^*$  and  $h_{33}^*$ , as is known from earlier studies (see, for instance, Refs. 21, 23 and 26).

Table 4 contains data on local maxima of  $h_{33}^*$  and  $k_t^*$  which are predicted for both the studied 1–2–2 composites. We can observe small differences between the maximum values of the parameter related to the araldite-containing and polyurethane-containing composites, Changes in the volume fraction  $m_s$  of *polymer I* in the laminar matrix do not lead to considerable changes in both  $k_t^*$  and  $h_{33}^*$ . This is mainly due to the relatively large volume fractions  $m_h$  and  $m_k$  at which local maxima of these parameters are achieved and at which the matrix does not strongly influence the piezoelectric properties of the 1–3-type composite. A comparison of the  $k_t^*$  and  $h_{33}^*$  values from Table 4 to the similar parameters of the KNNTL:Mn SC (see Table 1) enables us to state that an increase of  $k_t^*$  and  $h_{33}^*$  by approximately 1.9 and 1.4 times,

respectively, is achieved in a wide  $m_s$  range. Such a high performance in the 1–2–2 composites studied here is important for piezoelectric sensor, energy-harvesting and transducer applications.

#### 4 Comparison of results and discussion

This paper demonstrates that lead-free 1–2–2 composites reported here have a number of advantages over the composites based on the relaxor-FE SCs and FE ceramics. It can be seen from Table 5 that the composites based on the KNNTL:Mn SC exhibit large values of piezoelectric coefficients  $g_{33}^*$ ,  $h_{33}^*$  and  $g_h^*$ , and the thickness ECF  $k_t^*$  which are achieved at relatively small volume fractions of SC  $m$ . The validity of conditions (12) and (13) and the large anisotropy of the squared figures of merit  $(Q_{3j}^*)^2$  are also important characteristics that make the piezoelectric performance of the studied lead-free composites competitive in comparison to lead-containing composites based on the relaxor-FE SCs [21–23]. Among the factors that lead to these large parameters are the moderate dielectric permittivity  $\epsilon_{33}^\sigma$  of the KNNTL:Mn SC, the columnar architecture

**Table 4** Local maxima of the piezoelectric coefficient  $h_{33}^*$  (in  $10^{10} \text{ V}\cdot\text{m}^{-1}$ ) and thickness ECF  $k_t^*$  of 1–2–2 composites at  $m_s = \text{const}$

| $m_s$  | Local max $h_{33}^*$ | Volume fraction $m_h$ that corresponds to local max $h_{33}^*$ | Local max $k_t^*$ | Volume fraction $m_k$ that corresponds to local max $k_t^*$ |
|--|----------------------|--|-------------------|---|
| KNNTL:Mn SC / araldite / PE composite <sup>a</sup>     |                      |  |                   |   |
| 0.05   | 1.53                 | 0.855  | 0.937             | 0.571   |
| 0.10   | 1.53                 | 0.846  | 0.936             | 0.551   |
| 0.30   | 1.51                 | 0.821  | 0.930             | 0.505   |
| 0.50   | 1.50                 | 0.806  | 0.924             | 0.489   |
| 0.70   | 1.48                 | 0.794  | 0.916             | 0.493   |
| 0.90   | 1.47                 | 0.780  | 0.901             | 0.540   |
| KNNTL:Mn SC / polyurethane / PE composite <sup>b</sup> |                      |  |                   |   |
| 0.05   | 1.53                 | 0.862  | 0.937             | 0.585   |
| 0.10   | 1.53                 | 0.857  | 0.937             | 0.574   |
| 0.30   | 1.52                 | 0.841  | 0.933             | 0.547   |
| 0.50   | 1.51                 | 0.833  | 0.929             | 0.535   |

|      |      |       |       |       |
|------|------|-------|-------|-------|
| 0.70 | 1.50 | 0.819 | 0.924 | 0.537 |
| 0.90 | 1.49 | 0.807 | 0.913 | 0.550 |

<sup>a</sup> For the KNNTL:Mn SC / araldite / PE composite,  $m_s$  is the volume fraction of araldite in the laminar matrix

<sup>b</sup> For the KNNTL:Mn SC / polyurethane / PE composite,  $m_s$  is the volume fraction of polyurethane in the laminar matrix

of the composite and the elastic anisotropy of its laminar matrix with interfaces oriented perpendicular to the poling axis  $OX_3$  (see Fig. 1). The 1–2–2 composite based on the PMN–0.33PT SC is characterised by large squared figures of merit  $(Q_{33}^*)^2$  and  $(Q_h^*)^2$ , see Table 5. Their volume-fraction behaviour, as follows from the analysis of Eqs. (6) and (7), is mainly due to the very large piezoelectric coefficients  $d_{3j}$  of the PMN–0.33PT SC, see Table 1.

Results of our evaluations of the effective properties of the 1–2–2 composite at  $m = \text{const}$  and  $m_s = \text{const}$  are compared to those obtained for a similar 1–2–2 composite with a system of cylindrical SC rods and with the same arrangement of the main crystallographic axes in each rod (see Section 2). In the second stage of our evaluations, we used the effective field method [21] to calculate the effective properties of the composite wherein the cylindrical rods were surrounded by the laminar matrix. Differences between the parameters evaluated for the composite shown in Fig. 1 and for its analog with cylindrical SC rods do not exceed 2% in the wide volume-fraction range. We add that an important comparison of effective parameters evaluated for a 1–2–2 composite based on a relaxor-FE SC by means of the matrix and finite element methods was carried out in work [22], where good agreement between the results was observed.

The studied 1–2–2 composites based on the KNNTL:Mn SC have no analogs among the three-component piezo-active composites [21, 22, 27, 28] due to the combination of the large parameters (e.g.  $g_{33}^*$ ,  $h_{33}^*$  and  $g_h^*$ ) and the large anisotropy of the piezoelectric coefficients and ECFs [valid conditions (12) and (13)]. The

values of the piezoelectric coefficients  $g_{33}^*$  and  $g_h^*$  and related squared figures of merit  $(Q_{33}^*)^2$  and  $(Q_h^*)^2$  (Figs. 2–4) are a few times larger than the similar parameters of the 1–3-type, 2–2 and 3–3 composites based on FE ceramics of the PZT type [20, 28]. We add for a further comparison that the largest value of the thickness ECF  $k_t^*$  achieved in a 1–3 PMN–0.33PT SC / epoxy composite [29] is by 35% larger than  $k_t$  of its SC component.

In a 1–3-type composite wherein the PMN–0.33PT SC rods are surrounded by a porous araldite matrix, the effective parameters depend [23] on the volume fraction of SC and on the shape and volume fraction of air pores. For the case of heavily oblate spheroidal air pores with an aspect ratio 500 and porosity 30% in the araldite matrix, this composite is characterised by  $g_{33}^* = 522$  and  $g_h^* = 459$  (in  $\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ ),  $(Q_{33}^*)^2 = 1210$  and  $(Q_h^*)^2 = 934$  (in  $10^{-12} \text{ Pa}^{-1}$ ), and  $k_t^* = 0.943$  [23]. Maximum values of  $h_{33}^*$  of a 1–3 PMN–xPT SC / araldite composite studied in work [23] vary from  $0.261\cdot 10^{10} \text{ V}\cdot\text{m}^{-1}$  (at  $x = 0.30$ ) to  $0.569\cdot 10^{10} \text{ V}\cdot\text{m}^{-1}$  (at  $x = 0.42$ ). In comparison to this performance, the 1–2–2 KNNTL:Mn SC / araldite / PE composite is characterised by larger values of  $g_{33}^*$ ,  $g_h^*$  and  $h_{33}^*$ , see Tables 4 and 5. Moreover, a difference between values of  $\max k_t^*$  of the 1–3-type PMN–0.33PT-based composite from work [23] and local  $\max k_t^*$  of the 1–2–2 KNNTL:Mn-based composites (see Table 3) does not exceed 5%. It should be added that a 1–3 PMN–0.30PT SC / epoxy composite from work [30] is characterised by  $\max k_t^* \approx 0.8$  (experimental),  $\max g_{33}^* = 440 \text{ mV}\cdot\text{m}\cdot\text{N}^{-1}$  at  $m_{SC} = 0.018$  (calculated) and  $g_{33}^* = (80\text{--}120) \text{ mV}\cdot\text{m}\cdot\text{N}^{-1}$  at  $m_{SC} = 0.25\text{--}0.70$  (experimental). Here  $m_{SC}$  is the volume fraction of the [001]-poled PMN–0.30PT with the piezoelectric coefficient  $d_{33} \approx 1500 \text{ pC}\cdot\text{N}^{-1}$  [30]. This  $d_{33}$  value is approximately 2.8 times

larger than  $d_{33}$  of the KNNTL:Mn SC (see Table 1), however the aforementioned  $\max k_t^*$  and  $\max g_{33}^*$  values are smaller than the similar parameters of the 1-2-2 composites, see data in Figs. 2 a, c and 3 a, c, and Table 4. As follows from experimental data [20] on 1-3 niobate FE ceramic / epoxy composite, its  $\max k_t^* \approx 0.5$  and  $\max g_{33}^* \approx 240 \text{ mV}\cdot\text{m}\cdot\text{N}^{-1}$  are also smaller than those predicted for the studied 1-2-2 composites. The piezoelectric coefficient  $d_{33}$  of the poled niobate ceramic [20] is approximately 2.5 times smaller than  $d_{33}$  of the KNNTL:Mn SC.

The 1-2-2 composites based on the KNNTL:Mn SC have advantages over various FE materials. According to experimental results [7], a nanostructured Mn-modified  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$  polycrystalline ceramic is characterised by the squared figure of merit  $(Q_{33})^2 = 74.8 \cdot 10^{-12} \text{ Pa}^{-1}$ . This value is smaller than those predicted for  $(Q_{33}^*)^2$  of the 1-2-2 composites, see curves 1 and 3 in Fig. 4. However the anisotropy factor achieved for the Mn-modified  $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$  ceramic [7] is  $d_{33} / |d_{31}| \approx 21$ , therefore, the ratio  $(Q_{33})^2 / (Q_{31})^2 > 400$  is larger than  $(Q_{33}^*)^2 / (Q_{31}^*)^2$

related to the composite, see Fig. 5. In a modified  $\text{PbTiO}_3$  ceramic [1], the piezoelectric coefficients  $d_{33} = 56 \text{ pC}\cdot\text{N}^{-1}$  and  $g_{33} = 33 \text{ mV}\cdot\text{m}\cdot\text{N}^{-1}$  are smaller than those achieved in the studied KNNTL:Mn-based composites, however the anisotropy factor  $d_{33} / |d_{31}| = g_{33} / |g_{31}| = 8.2$  for the modified ceramic  $\text{PbTiO}_3$  is comparable to the similar anisotropy factors of the KNNTL:Mn-based composites; for instance, see the 9th column in Table 5. As follows from data for the KNNTL:Mn-based composite at  $m = 0.05$  and  $m_s = 0.30$  (see the first part of Table 5), the anisotropy factor  $g_{33}^* / |g_{31}^*| = 8.23$  is achieved at  $d_{33}^* = 259 \text{ pC}\cdot\text{N}^{-1}$  and  $g_{33}^* = 1480 \text{ mV}\cdot\text{m}\cdot\text{N}^{-1}$ , i.e., we observe obvious advantages of the lead-free composite over the typical  $\text{PbTiO}_3$ -based ceramic from work [1]. A grain-oriented and highly textured modified  $\text{PbTiO}_3$  material manufactured by Yan et al. [31] is characterised by the piezoelectric coefficient  $g_{33} = 115 \text{ mV}\cdot\text{m}\cdot\text{N}^{-1}$ , and this value is by a few times smaller than  $g_{33}^*$  of the studied 1-2-2 lead-free composites, see Figs. 2 a, c and 3 a, c.

In Table 6 we show examples of the performance of the textured lead-free FE

**Table 5** Comparison of effective parameters of 1-2-2 composites based on [001]-poled domain-engineered SCs

| $m$                                     | $m_s$ | $g_{33}^*,$<br>$\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ | $g_h^*,$<br>$\text{mV}\cdot\text{m}\cdot\text{N}^{-1}$ | $(Q_{33}^*)^2,$<br>$10^{-12} \text{ Pa}^{-1}$ | $(Q_h^*)^2,$<br>$10^{-12} \text{ Pa}^{-1}$ | $h_{33}^*,$<br>$10^{10} \text{ V}\cdot\text{m}^{-1}$ | $k_t^*$ | $\frac{g_{33}^*}{ g_{31}^* }$ | $\frac{(Q_{33}^*)^2}{(Q_{31}^*)^2}$ | $\frac{h_{33}^*}{ h_{31}^* }$ | $\frac{k_t^*}{ k_p^* }$ |
|---|-------|---|--|---|--|--|---------|-------------------------------|-------------------------------------|-------------------------------|-------------------------|
| KNNTL:Mn SC / araldite / PE composite   |       |   |  |   |  |  |         |                               |                                     |                               |                         |
| 0.05                                    | 0.10  | 1550  | 980  | 449   | 179  | 0.928  | 0.845   | 6.76                          | 45.6                                | 140                           | 4.81                    |
|   | 0.20  | 1520  | 1020   | 416   | 186  | 0.910  | 0.835   | 7.81                          | 60.9                                | 103                           | 4.80                    |
|   | 0.30  | 1480  | 1010   | 383   | 178  | 0.890  | 0.823   | 8.23                          | 67.7                                | 82.4                          | 4.57                    |
| 0.10                                    | 0.10  | 869   | 512  | 333   | 116  | 1.17   | 0.899   | 6.07                          | 36.8                                | 158                           | 5.18                    |
|   | 0.20  | 862   | 537  | 318   | 124  | 1.16   | 0.894   | 6.88                          | 47.3                                | 115                           | 5.04                    |
|   | 0.30  | 854   | 543  | 303   | 122  | 1.14   | 0.887   | 7.20                          | 51.9                                | 91.1                          | 4.73                    |
| 0.30                                    | 0.10  | 309   | 135  | 152   | 29.1                                       | 1.43   | 0.931   | 4.00                          | 16.0                                | 150                           | 4.50                    |
|   | 0.20  | 309   | 143  | 149   | 32.2                                       | 1.42   | 0.929   | 4.26                          | 18.2                                | 109                           | 4.09                    |
|   | 0.30  | 308   | 146  | 147   | 33.0                                       | 1.41   | 0.926   | 4.37                          | 19.0                                | 85.1                          | 3.73                    |
| PMN-0.33PT SC / araldite / PE composite |       |   |  |   |  |  |         |                               |                                     |                               |                         |
| 0.05                                    | 0.10  | 666   | 438  | 671   | 290  | 0.363  | 0.878   | 5.84                          | 34.1                                | 514                           | 3.46                    |
|   | 0.20  | 655   | 455  | 613   | 295  | 0.362  | 0.870   | 6.51                          | 42.4                                | 372                           | 3.38                    |
|   | 0.30  | 643   | 454  | 557   | 278  | 0.361  | 0.860   | 6.81                          | 46.3                                | 291                           | 3.22                    |
| 0.10                                    | 0.10  | 361   | 221  | 547   | 205  | 0.376  | 0.916   | 5.15                          | 26.6                                | 486                           | 3.40                    |
|   | 0.20  | 358   | 231  | 513   | 214  | 0.375  | 0.911   | 5.65                          | 32.0                                | 353                           | 3.24                    |
|   | 0.30  | 354   | 233  | 479   | 208  | 0.374  | 0.905   | 5.86                          | 34.3                                | 276                           | 3.05                    |
| 0.30                                    | 0.10  | 127   | 57.1   | 291   | 58.9                                       | 0.384  | 0.941   | 3.64                          | 29.1                                | 380                           | 2.90                    |
|   | 0.20  | 187   | 104  | 367   | 114  | 0.384  | 0.932   | 4.52                          | 20.5                                | 276                           | 2.93                    |
|   | 0.30  | 126   | 61.5   | 275   | 65.2                                       | 0.383  | 0.935   | 4.19                          | 15.2                                | 216                           | 2.43                    |

ceramics [32]. The  $g_{33}$  and  $(Q_{33})^2$  values listed in Table 6 are smaller than the similar parameters of the studied 1–2–2 composites (see Figs. 2–4), and the piezoelectric coefficient  $d_{33}$  of the ceramics is comparable to  $d_{33}^*$  of the 1–2–2 composites at relatively small volume fractions of SC  $m$ .

## 5 Conclusion

We present the first detailed study of lead-free 1–3-type composites and their effective parameters for piezoelectric

**Table 6** Room-temperature properties and squared figures of merit of poled textured  $(K_xNa_{1-x})_{0.946}Li_{0.054}NbO_3$  ceramics<sup>a</sup>

| $x$   | $d_{33}$ , pC·N <sup>-1</sup> | $\varepsilon_{33}^{\sigma} / \varepsilon_0$ | $g_{33}$ , mV·m·N <sup>-1</sup> | $(Q_{33})^2$ , 10 <sup>-12</sup> Pa <sup>-1</sup> |
|-------|-------------------------------|---|---------------------------------|---|
| 0.410 | 236                           | 533   | 50.0                            | 11.8  |
| 0.427 | 231                           | 601   | 43.4                            | 10.0  |
| 0.445 | 252                           | 606   | 47.0                            | 11.8  |
| 0.463 | 254                           | 646   | 44.4                            | 11.3  |

<sup>a</sup> From experimental results [32]

transducer and related applications. This includes the analysis of the piezoelectric properties and related parameters of lead-free composites with 1–2–2 connectivity, whose structure is shown in Fig. 1. The main piezo-active component is the [001]-poled KNNTL:Mn SC that exhibits large piezoelectric properties and electromechanical coupling, see data in Table 1. The SC rods in the composite sample are surrounded by the laminar polymer matrix with 2–2 connectivity. Such a matrix is of interest due to the elastic properties and their strong influence on the hydrostatic parameters and anisotropy factors of the 1–2–2 composite. The unique advantages of the studied 1–2–2 composites over conventional lead-based FE ceramic / polymer and modern relaxor-FE SC / polymer composites and many FE ceramics are the large values of the piezoelectric coefficients  $g_{33}^*$ ,  $g_h^*$  and  $h_{33}^*$  and thickness ECF  $k_t^*$ , the large anisotropy of the squared figures of merit  $(Q_{3j}^*)^2$ , and the relatively large hydrostatic squared figures of merit  $(Q_h^*)^2$ .

Conditions (12) and (13) for the large anisotropy of the piezoelectric coefficients and ECFs, respectively, are valid in specific ranges of the volume fractions  $m$  and  $m_s$ , see Fig. 7. It has been shown that the araldite / PE matrix with the larger difference of the elastic properties of *polymers I* and *II* leads to the simultaneous validity of conditions (12) and (13) as well as larger values of the piezoelectric coefficient  $g_h^*$  of the composite. Important correlations between the  $s_{33}^{(m)} / s_{13}^{(m)}$  and  $d_{33}^* / d_{31}^*$  ratios and between the  $s_{anis}$  factor and  $k_t^* / k_p^*$  ratio (Table 3) have been initially found and described by interpretation of the validity of conditions (12) and (13) at  $m \ll 1$  (Fig. 7), i.e., when an influence of the SC rods on the piezoelectric performance of the composite remains weak.

The presented parameters and advantages of the studied lead-free 1–3-type composites enable us to conclude that these materials can be used as active elements of modern piezoelectric sensors (with large  $g_{33}^*$ ,  $(Q_{33}^*)^2$ ,  $h_{33}^*$ ,  $(Q_{33}^*)^2 / (Q_{31}^*)^2$ , etc.), transducers and energy-harvesting devices (with large  $k_t^*$ ,  $k_t^* / |k_p^*|$ ,  $d_{33}^* / |d_{31}^*|$ ,  $(Q_{33}^*)^2$ , and  $(Q_{33}^*)^2 / (Q_{31}^*)^2$ ), hydrophones (with large  $g_h^*$  and  $(Q_h^*)^2$ ), and other piezotechnical devices.

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